
**STOPPING
WATER POLLUTION
AT ITS SOURCE**



**ST. CLAIR RIVER MISA
PILOT SITE INVESTIGATION**

**VOLUME II
PART I – TECHNICAL SUMMARY**



**Environment
Ontario**

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ST. CLAIR RIVER MISA PILOT SITE INVESTIGATION

VOLUME II
PART I - TECHNICAL SUMMARY

Prepared by the
St. Clair River MISA Pilot Site Team

JANUARY 1991



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EXECUTIVE SUMMARY

BACKGROUND

In June 1986 the Ontario Ministry of the Environment (MOE) embarked upon an ambitious and comprehensive pollution abatement program with the release of the White Paper, entitled "Municipal-Industrial Strategy for Abatement (MISA) - A Policy and Program Statement of the Government of Ontario on Controlling Municipal and Industrial Discharges into Surface Waters".

The White Paper provides the framework for the control of toxic contaminants in industrial and municipal effluents; initially, through a regulatory component to enforce technology-based effluent limits. The minimum pollution control requirement will be based upon the implementation of "best available technology economically achievable" (BATEA). As treatment technologies are advanced, BATEA requirements will be adjusted, moving towards the goal of virtual elimination of persistent toxic contaminants. This is a concept consistent with the policies stated in the 1987 Revised Great Lakes Water Quality Agreement.

Development of these controls will be accomplished through the promulgation of Effluent Monitoring Regulations and Effluent Limits Regulations directed at municipal and industrial sectors in order to achieve water pollution control at its source.

The MISA program will also provide information which will assist in the development of long-term Remedial Action Plans (RAPs) for the Great Lakes Areas of Concern identified by the International Joint Commission.

Given that protection of the environment is fundamental to the MISA initiative, the MOE continues to develop site-specific, receiving water-based effluent limits, to protect environmentally sensitive areas. Some of these areas may require more stringent limits than those prescribed by MISA regulations to protect local water quality. Effluent requirements based on receiving-water conditions are derived using sophisticated

modelling techniques which establish a predictive link between effluent quality and specific effects on the aquatic environment. Models will augment current narrative methods for establishing effluent limits.

In order to adopt standard procedures for the derivation of receiving-water-based effluent limits, the MOE has evaluated numerous traditional and novel water quality assessment techniques. These techniques have been applied on a site-specific basis at six "Pilot Sites" throughout Ontario, to assess their suitability in establishing receiving-water-based effluent limits.

Six Pilot Sites were selected to provide a cross-section of industrial and municipal dischargers and receiving-water environments existing in Ontario. The six sites, and the principal dischargers studied, are as follows:

- (1) Kaministiquia River at Thunder Bay (Canadian Pacific Forest Products, formerly Great Lakes Forest Products)
- (2) St. Marys River at Sault Ste. Marie (Algoma Steel)
- (3) St. Clair River at Sarnia (Dow Chemical)
- (4) Grand River at Waterloo (Waterloo Sewage Treatment Plant [STP])
- (5) Lake Ontario at Toronto (Toronto Main STP) ,
- (6) St. Lawrence River at Cornwall (several municipal and industrial sources).

Two distinct goals were expressed at the outset of these Pilot Site investigations, which were initiated in 1986. These goals are:

- To develop site-specific effluent requirements for hazardous and conventional pollutants from specific dischargers, based on receiving-water impact assessment.
- To develop and document, for application to other comparable discharger and receiving-water situations in the province, an acceptable set of receiving-water assessment techniques and procedures.

STUDY OUTLINE AND RATIONALE

This Executive Summary provides an overview of findings from specific studies in the St. Clair River primarily undertaken from May 1986 to March 1987 and again in May 1988 to assess the impacts of discharges from Dow Chemical Canada Inc. (Dow) on the river, both locally and downstream. Dow was selected as an example of a petrochemical industry discharging to a Great Lakes connecting channel. In order to distinguish the effects of sources at Dow from upstream sources, additional sampling occurred at the Cole drain and Polysar Ltd. (Sarnia). As a result, specific impacts from the upstream sewers were also evaluated at a level of detail similar to that applied at Dow.

The final Pilot Site report is comprised of three parts: a Technical Summary (including this Executive Summary), Detailed Technical Findings; and Appendices.

To establish a link between point-source discharges of toxic contaminants and effects on the receiving environment, a marriage of state-of-the-art modelling techniques and environmental assessment methods was necessary. The ambient water-quality conditions necessary to meet established criteria for the protection of aquatic life were determined. Predictive modelling was then used to determine the end-of-pipe concentrations necessary to meet these conditions.

MOE water-quality Objectives/Guidelines were used where available. For those substances where the MOE has not specified an ambient limit, the requirements of other agencies were used. Where no definitive limits were available from either the MOE or other agencies, water quality "advisories" were developed by the Water Resources Branch of the MOE. As aquatic toxicity data are normally limited for such substances, large safety factors had to be built in to these advisories. As additional toxicity information becomes available, advisories will be adjusted to reflect an improved database.

The St. Clair River Pilot Site Study investigated the presence and effects of 66 organic compounds and metals in the final discharges from six sewers at Dow Chemical Canada Inc. (Sarnia), two outfalls at Polysar Ltd. (Sarnia), and the Cole drain.

Eight chemicals of concern were selected for detailed study due to their documented presence in industrial effluents and potential hazard to the environment. These included seven organic compounds and mercury. The organic chemicals included some lower molecular weight, volatile organic compounds, namely carbon tetrachloride (CCL4) and tetrachloroethylene (PERC), and some chlorinated aromatic compounds, namely hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), hexachloroethane (HCE), octachlorostyrene (OCS) and 2,4,5-trichlorotoluene (2,4,5-TCT).

The chemical fate and transport model WASTOX (Water Quality Analysis Simulation for Toxics), developed by Dr. J.P. Connolly of Manhattan College and modified for use by the MOE, enabled the accurate prediction of contaminant distribution in the St. Clair River ecosystem. Through the use of WASTOX, other sophisticated mathematical models and a comprehensive sample collection effort, effluent limits (load allocations) were derived for evaluation purposes based on water and sediment quality as well as the health of the biological community.

The effluent limits recommended in this report were derived only through water-quality-based models, given that sediment- and biologically-based models require further refinements, additional data, and the development of appropriate receiving-water-based criteria.

CONCLUSIONS AND RECOMMENDATIONS

The St. Clair River Pilot Site Study makes specific recommendations for maximum allowable chemical-specific load allocations for selected point-source discharges to the St. Clair River. Required reductions for chemicals of concern vary from not exceeding the loadings measured in 1986-87 to a 99.8% reduction for octachlorostyrene at the Cole drain. For

the overall Dow Chemical complex, recommended reductions for hexachlorobenzene and octachlorostyrene are 75% and 99% respectively, whereas recommended reductions for tetrachloroethylene and hexachlorobutadiene are 39% and 13%.

With the exception of OCS, existing loads from the Polysar 72-inch sewer were sufficiently low to ensure the protection of aquatic life, while several contaminants of concern emitted at the Cole drain require further reductions. Table 1 identifies recommended loads and reductions necessary to maintain acceptable environmental conditions at the edge of the mixing zone, based on measurements made during 1986 and 1987.

Extensive effluent monitoring indicates that most sewers demonstrate highly variable effluent quality, with occasional peak discharges accounting for a disproportionately high fraction of annual loadings. Findings indicate that minimizing this variability in effluent quality would assist in achieving compliance with effluent guidelines.

Notwithstanding recommended reductions, it is recognized that loadings of total volatile organic compounds and chlorinated aromatic compounds to the St. Clair River from Dow Chemical Inc. were significantly reduced from November 1985 to the end of March 1987. Dow facility loadings were reduced in the order of 90% and 76% for these two groups of compounds respectively.

Additional effluent monitoring now being conducted under MISA at Dow and Polysar will verify sewer and facility load reductions to the St. Clair River, and will be used to evaluate the effectiveness of specific in-plant remedial measures.

It was determined through long-term effluent monitoring that both the Cole drain and the Dow 42-inch sewer are significant sources of the parameters of concern including HCB, HCBd, HCE and OCS.

TABLE 1: SUMMARY OF RECEIVING-WATER-BASED LOAD ALLOCATIONS
FOR 95% COMPLIANCE TARGET*

MEAN MONTHLY LOADS (g/d)								
SOURCE	OCS	HCB	2,4,5 - TCT	HCBD	HCE	PERC	CCL4	Hg
<u>Cole drain:</u>								
Existing	9.2	8.9	9.6	140	6.8	48	7.9	2.2
Recommended	0.015W	3.9W	9.6E	87W	6.8E	48E	7.9E	2.2E
% reduction	99.8	56.2	0	37.9	0	0	0	0
<u>Polysar 72-inch</u>								
Existing	0.2	0.1	0.001	1	0.1	6.9	2.7	0.4
Recommended	0.002W	0.1E	0.001E	1E	0.1E	6.9E	2.7E	0.4E
% reduction	99.5	0	0	0	0	0	0	0
<u>Dow 1st Street:</u>								
Existing	3.1	7.5	50	31	80	2190	2972	4.4
Recommended	0.039W	1.7W	34W	26W	80E	1000W	2972E	4.4E
% reduction	98.7	77.3	32	16.1	0	54.3	0	0
<u>Dow 2nd Street:</u>								
Existing	0.3	1	1.9	4	1.5	153	188	2.8
Recommended	0.001W	.8W	1.9E	4E	1.5E	153E	188E	2.8E
% reduction	99.7	20	0	0	0	0	0	0
<u>Dow 3rd Street:</u>								
Existing	0.1	0.1	.2	1.9	0.4	25	254	2.7
Recommended	0.001W	0.1E	.2E	1.7W	0.4E	25E	254E	2.7E
% reduction	99.0	0	0	10.5	0	0	0	0
<u>Dow 4th Street:</u>								
Existing	0.5	3.3	1.4	4.7	36.2	684	676	6.4
Recommended	0.005W	0.4W	1.4E	4.7E	36.2E	684E	676E	6.4E
% reduction	99.0	87.9	0	0	0	0	0	0

Existing (E) = Existing mean monthly load; **Recommended** = allocated mean monthly load; % reduction = recommended vs. existing; W = modelled load allocation utilizing receiving-water-based (water-quality) model

Note: Dow 1st Street includes 42-, 48- and 54-inch sewers.

* Compliance Target is fraction of time for which effluent limits must be met based on water-quality model.

Specific remedial measures for reducing contaminant loadings to the St. Clair River must be undertaken in the Cole drain catchment basin and in the waste streams entering the Dow 42-inch sewer, in order to achieve the recommended receiving-water-based effluent limits.

Ambient water sampling, sequential sampling, long-term effluent monitoring, juvenile fish collections, and centrifuging data in support of the model calibration, were found to be essential assessment techniques for setting receiving-water-based effluent limits.

Biomonitoring data indicate that the benthic community habitat has improved substantially since the late 1970's resulting in a reduction of the "impaired" zone from 21 to 12 km downstream from the Polysar/Dow site by 1985 with further improvements noted in 1986.

In addition to the on-going sportfish contaminant testing program, regular biomonitoring of the benthic community and young-of-the-year fish are to be continued to document the effectiveness of further remedial measures.

Continued efforts must be expended to develop PWQOs for those parameters of concern for which there are currently no MOE-endorsed Provincial Water Quality Objectives. The availability of toxicity data through ongoing and proposed government and industry initiatives will enable the development of PWQOs and Provincial Water Quality Guidelines (PWQGs) with a higher degree of confidence and more appropriate safety factors. The timely development of Provincial sediment quality and contaminant residue in biota guidelines must also be ensured.

Average levels of HCB in sportfish samples collected in 1985-1987 did not exceed a human health guideline established by Health and Welfare Canada for the consumption of whole chicken eggs; however, carp and channel catfish collected from Lake St. Clair exceeded existing U.S. EPA consumption guidelines for the protection of human health.

Priority consideration must be given to the development of biota-based effluent limits to protect the general population, with special consideration to local communities such as the Walpole Island First Nation Indian Community, who consume large quantities of locally caught fish.

The findings of this study will ultimately be used in concert with the treatment technology-based effluent requirements (MISA-BATEA) to ensure adequate protection of the aquatic ecosystem. The eventual availability of point-source loading data from Dow and Polysar as part of the MISA Effluent Monitoring Regulation will highlight the effectiveness of remedial measures undertaken by Dow and Polysar during and subsequent to this study.

The procedures for the derivation of receiving-water-based effluent limits presented in this Pilot Site investigation are not static. They are flexible to allow utilization of new and more substantive information as it becomes available. In addition, the assessment techniques and modelling applications can be used in similar receiving-water environments throughout the Province.

This document will serve as a useful reference for the Ministry of the Environment and its clients in establishing site-specific, receiving-water-based effluent limits for hazardous and conventional pollutant discharges.

ACKNOWLEDGEMENTS

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Initial direction, planning and coordination was provided by Mr. Y.S. Hamdy of the Water Resources Branch. His keen foresight enabled the development of the novel yet workable investigative techniques.

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The text was typed by a number of individuals from the Water Resources Branch including V.E. Sokolyk, E. Lacson, C. Fong, L. Satya, L. Matar and A. Foley.

PILOT SITE TEAM MEMBERS

The St. Clair River MISA pilot site team consisted of:

G. Johnson*, Coordinator, Water Resources Branch, MOE

S. Abernethy, Water Resources Branch, MOE

R. Boone, Water Resources Branch, MOE

D. Edwardson, Detroit, St. Clair, St. Marys River Improvement Team, MOE

R. Griffiths, Southwestern Region, MOE

K. Haniff, Detroit, St. Clair, St. Marys River Improvement Team, MOE

B. Hawkins, Southwestern Region, MOE

A. Hayton, Water Resources Branch, MOE

M. Jackson, Water Resources Branch, MOE

A. Johnson, Water Resources Branch, MOE

J. Lee, Water Resources Branch, MOE

T. Lomas, Water Resources Branch, MOE

J. Luyt, Sarnia Area, MOE

J. A. McCorquodale, University of Windsor

P. Nettleton, Water Resources Branch, MOE

A. Mudroch**, National Water Research Institute, DOE

A. Rodrigues, Water Resources Branch, MOE

D. Rokosh, Water Resources Branch, MOE

W. Scheider, Water Resources Branch, MOE

K. Suns, Water Resources Branch, MOE

S. Thornley, Southwestern Region, MOE

D. Veal, Southwestern Region, MOE

G. Westlake, Water Resources Branch, MOE

* Replaced Y. Hamdy

** Replaced K. Rodgers

SYNTHESIS TEAM MEMBERS

The following individuals comprised the synthesis writing team and were responsible for writing and for assembling significant portions of the final report.

G. Johnson - Editor

R. J. Boone

J. A. McCorquodale

P. Nettleton

W. Scheider

D. Veal

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1.0 INTRODUCTION

1.1 Overview of the MISA Initiative

Since the June 1986 release of the Ministry of the Environment's (MOE) White Paper, entitled "Municipal-Industrial Strategy for Abatement" (MISA), a comprehensive abatement program has been under development to establish regulations for controlling water pollution at its source.

The White Paper provides the framework for the control of toxic contaminants in industrial and municipal effluents; initially, through a regulatory component to enforce technology-based effluent standards. The minimum pollution control requirement will be based upon implementation of best available technology economically achievable (BATEA).

Development of these controls will be accomplished through the promulgation of two regulations:

- (1) the Effluent Monitoring Regulation, requiring dischargers to measure concentrations and loadings of toxic contaminants in their effluents, as specified in the Ontario Effluent Monitoring Priority Pollutants List (EMPPL); and
- (2) the Limits Regulation, specifying maximum permitted loadings of toxic pollutants for point-source dischargers.

Where necessary, in environmentally sensitive areas, technology-based effluent limits will be compared with site-specific, receiving-water-based effluent limits. The site-specific limits will consider the environmental sensitivity of water bodies, where more stringent limits than those prescribed by BATEA may be required.

1.2 Development of Receiving-Water-Based Effluent Limits

To assist in developing standard procedures for the derivation of receiving-water-based effluent limits, the Ministry has evaluated numerous traditional and novel water quality assessment techniques. These

techniques have been applied on a site-specific basis at six "Pilot Sites" throughout Ontario, to determine their suitability in establishing receiving-water-based effluent limits.

The six Pilot Sites were selected to provide a cross-section of industrial/municipal dischargers and receiving-water environments existing in Ontario. The six sites, and the principal dischargers studied, are as follows:

- (1) Kaministiquia River at Thunder Bay (Canadian Pacific Forest Products, formerly Great Lakes Forest Products)
- (2) St. Marys River at Sault Ste. Marie (Algoma Steel)
- (3) St. Clair River at Sarnia (Dow Chemical)
- (4) Grand River at Waterloo (Waterloo Sewage Treatment Plant [STP])
- (5) Lake Ontario at Toronto (Toronto Main STP)
- (6) St. Lawrence River at Cornwall (Several Municipal and Industrial Sources)

As a basis for determining the impacts of toxic contaminants on the aquatic environment, the Pilot Site study teams have relied on Provincial Water Quality Objectives (PWQO's), Guidelines (PWQG's), advisories, as well as water- and biologically-based criteria developed by other government agencies, to determine acceptable conditions.

Water quality "advisories" are values which have been developed to protect aquatic life based on a very limited amount of toxicological information. The Ministry has developed a hierarchical protocol for developing water quality Objectives (PWQOs); Guidelines (PWQGs) and advisories based on a descending level of available chronic and acute toxicity information. The safety factors applied in deriving PWQO, PWQG and advisories may range from 10 to 9,000 depending on the amount of toxicological information available.

To establish and simulate the cause-effect relationships between source and receiver, these studies have built upon classical and newly verified biological and modelling assessment techniques to account for the complex behaviour of some of these toxic compounds.

1.3 The St. Clair River MISA Pilot Site Study

This report incorporates specific studies undertaken in the St. Clair River (Figures 1a, b, c) from May 1986 to May 1988 to assess the impacts of discharges from Dow Chemical Canada Inc. (Dow) on the river, both locally and downstream. In order to discriminate the effects of sources at Dow from potential upstream sources, additional sampling occurred at the Cole drain and Polysar Ltd. (Sarnia). As a result, specific impacts from the upstream sewers were also evaluated at a level of detail similar to that applied at Dow.

Scientific investigations have included sampling at selected outfalls in the area, coupled with water and sediment quality sampling and biomonitoring of the entire St. Clair River.

Data collected from these studies have been used for calibrating and subsequently verifying state-of-the-art predictive fate and transport models. These models were applied to determine the toxic contaminant distribution in the St. Clair River.

The studies were designed to evaluate the impacts of chemicals of concern discharged to the St. Clair River, in order to fulfill the two primary goals of this investigation:

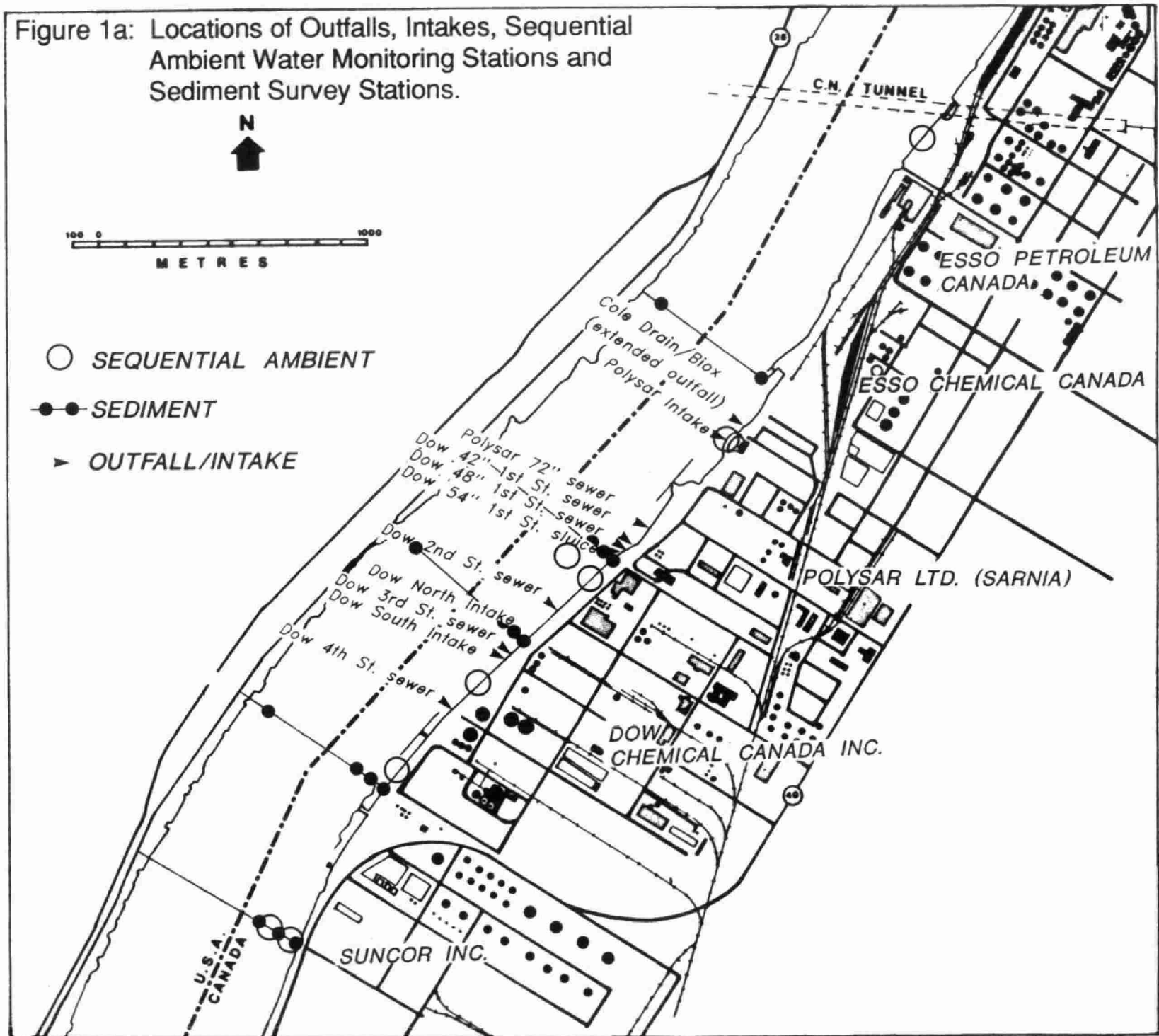
- (1) Develop site-specific effluent requirements for hazardous and conventional pollutants from designated discharges on the St. Clair River, based on receiving-water impact assessments.
- (2) Develop and document, for application to other comparable discharger and receiving-water situations in the Province, an acceptable set of receiving-water assessment techniques and procedures.

1.4 Study Outline

1.4.1 Focus and Rationale

The St. Clair River Pilot Site Study investigated the presence and effects of selected organic compounds and some metals in the final

Figure 1a: Locations of Outfalls, Intakes, Sequential Ambient Water Monitoring Stations and Sediment Survey Stations.



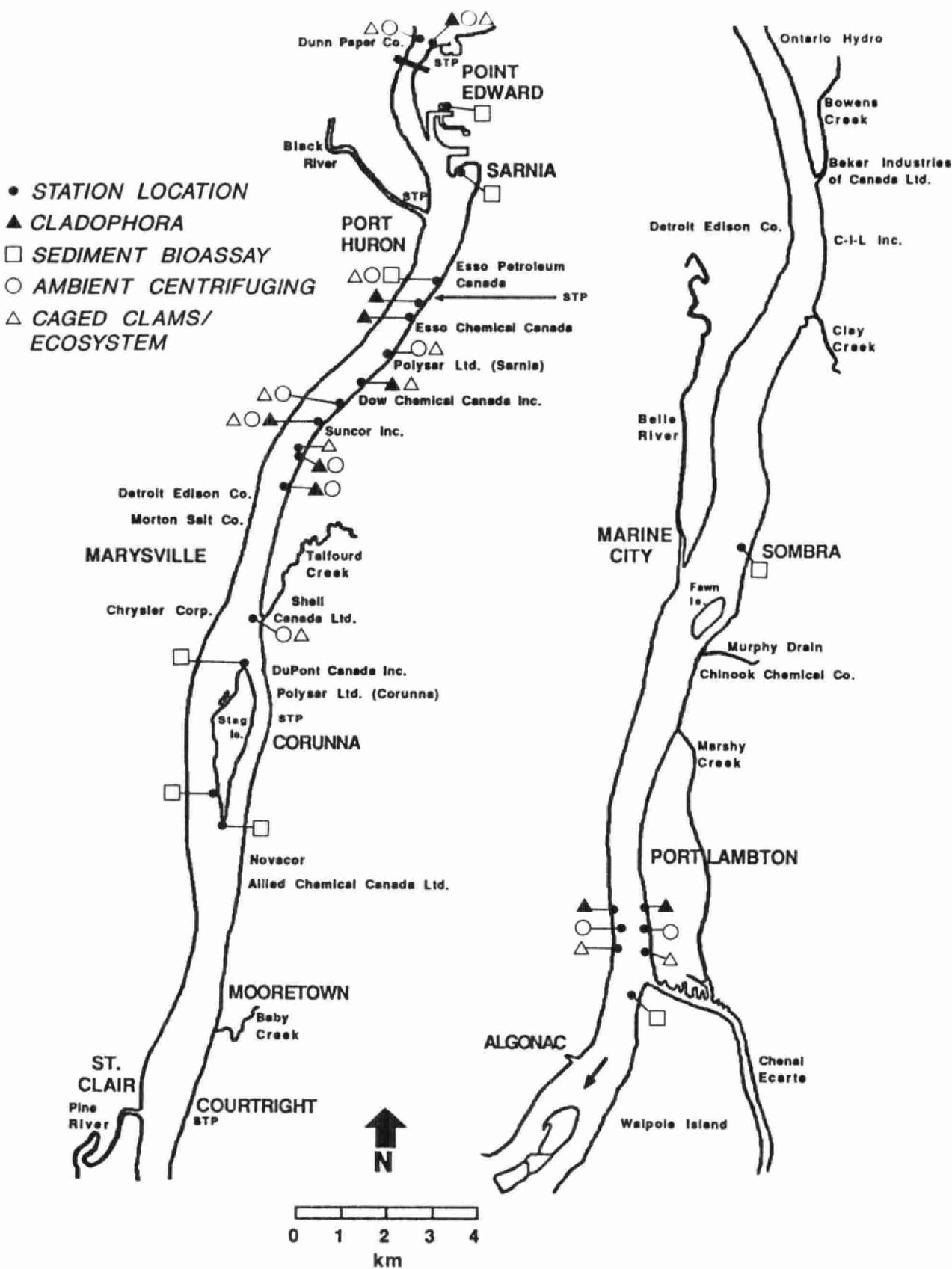


Figure 1b: Locations of Biomonitoring and Sediment Bioassay Stations.

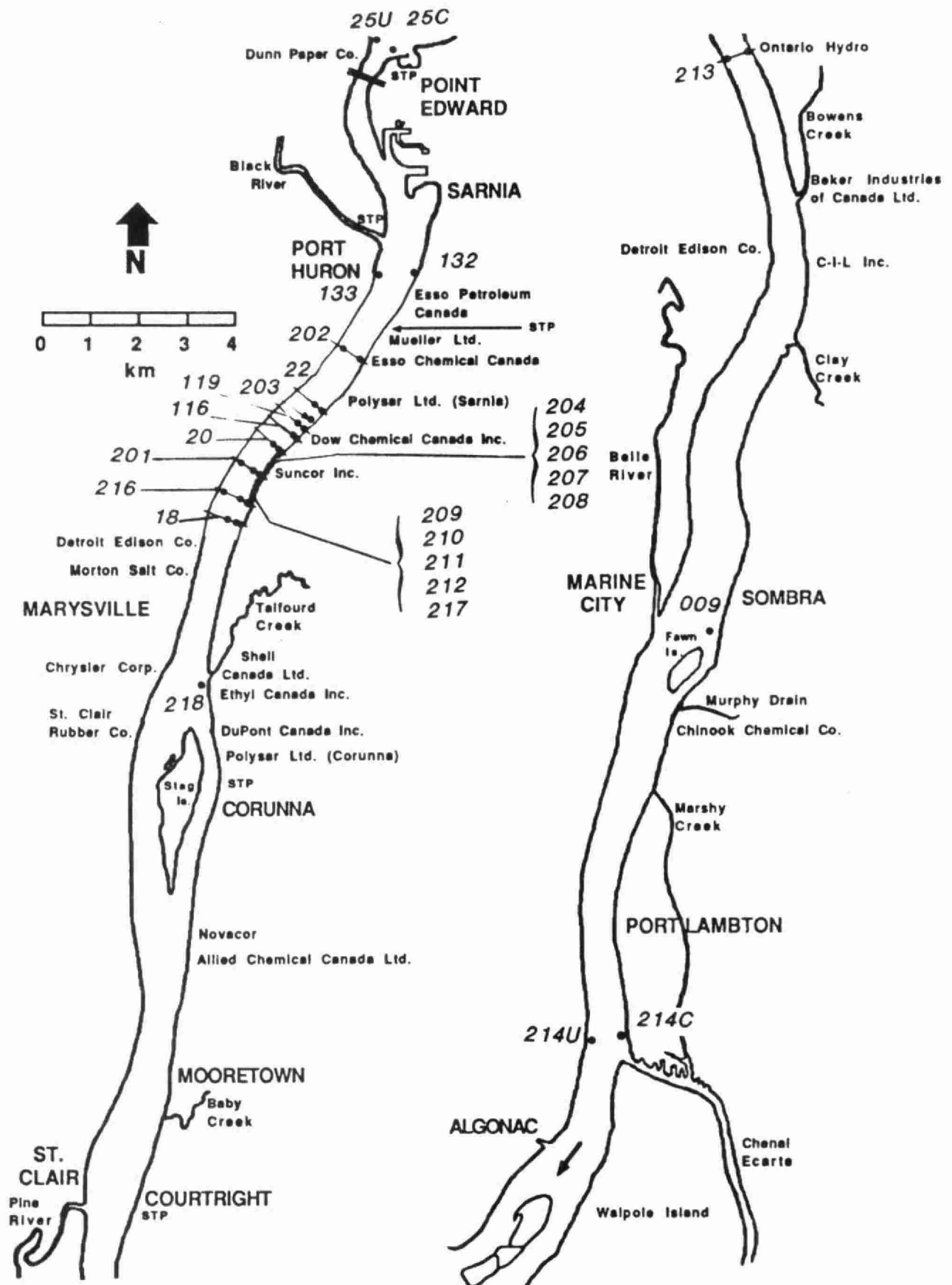


Figure 1c: Ambient Water Investigative Sampling Locations.

discharges from six sewers at Dow Chemical Canada Inc., and two outfalls at Polysar Ltd. in addition to the Cole drain (Figure 1a).

The study focused on eight "parameters of potential concern". These included seven organic compounds and mercury. The organic chemicals included some lower molecular weight, volatile organic compounds, namely carbon tetrachloride (CCL4) and tetrachloroethylene (PERC) and some chlorinated aromatic compounds, namely hexachlorobenzene (HCB), hexachlorobutadiene (HCBd), hexachloroethane (HCE), octachlorostyrene (OCS) and 2,4,5-trichlorotoluene (2,4,5-TCT). These chemicals were selected because they are intermediate- or end-products from organic chemical manufacturing processes. Existing data-bases for these substances have demonstrated consistently detectable levels in industrial effluents discharging to the St. Clair River, over a number of years. Most of these chemicals also tend to bioaccumulate in aquatic organisms and some have demonstrated potential mutagenic or carcinogenic activity in laboratory experiments.

The study also focused on mercury which tends to bioaccumulate in its methylated form. This contaminant, responsible for the imposition of fish consumption advisories in Lake St. Clair during the 1970's, was considered in order to determine the significance of current sources compared to in-place or historical contamination.

1.4.2 Ecosystem Approach

The Pilot Site investigation was designed to develop a holistic understanding of the response of the St. Clair River ecosystem to chemical discharges from Dow, and at the same time, discriminate effects from Polysar and the Cole drain. As part of this ecosystem approach, water, sediment and biota were studied with the ultimate goal of creating an ecosystem-chemical-response model, capable of simulating the distribution of contaminants between chemical discharges and the aquatic ecosystem. This model would then establish the link between the actual amount of discharged chemicals and the effect of the discharge on receiving-water-quality, sediment-quality and contaminant burdens in biota.

The Pilot Site investigation contained three main field study components:

(1) An assessment of contaminants in water, sediment and biota of the St. Clair River ecosystem:

These investigative components were designed to assess the impact of present discharges on various ecosystem components; to develop and improve monitoring procedures and to provide data for the calibration and verification of environmental fate and transport models.

(2) Several short-interval, sequential effluent and water monitoring studies.

These component studies were designed to assess cause and effect relationships between the effluent and the receiving environment. Additionally, the sampling program enabled the calibration and verification of environmental fate and transport models in the vicinity of the outfalls and the assessment of the ecosystem responses and load variability. Short-term sequential sampling (half-hourly sampling for 7 hours) occurred in close proximity to industrial outfalls, while an extensive 43 station water sampling grid was established along the entire river length.

(3) Long-term monitoring of effluents:

This monitoring program established monthly loading rates and the temporal variability in loading rates through twice-weekly sampling for an 11-month period. It also enabled tracking of the effects of remedial measures.

2.0 OVERVIEW OF FINDINGS

2.1 Sequential Sampling

Three cruises involving sequential effluent sampling at half-hourly intervals demonstrated a high degree of short-term variability in the effluent loads. This variability in mass loadings is a reflection of fluctuating concentrations given that sewer discharge rates did not change significantly during the study. The three cruises were carried out as follows:

- (1) Spring 1986 (May)
- (2) Summer 1986 (June)
- (3) Fall 1986 (October)

In each cruise, the waters in the vicinity of Dow, Polysar and the Cole drain sites, as far downstream as Suncor were sampled sequentially at the same intervals as the outfalls. These data were used to calibrate and to verify the mathematical exposure models.

The sequential sampling program involved simultaneous measurements of effluent and water concentrations. The major loads of HCB, OCS, HCBd, 2,4,5-TCT, HCE, CCL4 and PERC were observed at the Cole drain and at the Polysar and Dow outfalls. The water concentrations reflected these sources as each of these parameters was below detection levels upstream from the Cole drain, while concentrations downstream from this area approached or exceeded several water-quality criteria.

2.1.1 Loads and Short-Term Load Variability

The study demonstrated a considerable short-term variability in the contaminant loads. For example, a 1000-fold variation between maximum and minimum loads of HCB was determined for the Dow 1st Street 42-inch sewer. An index to the load variability is the ratio of the load that is exceeded 5 per cent of the time (i.e. extreme load), to the mean

load; this ratio was approximately 11 for HCB at the Dow 1st Street 42-inch sewer. The same phenomenon was observed at all the Dow and Polysar sewers and at the Cole drain.

2.1.2 Nearfield Concentrations

The variability of the chemical concentrations in the river water in the immediate vicinity of the major outfalls was similar to the effluent load variability. This nearfield variability decreased significantly with increasing distance downstream, and from the Ontario shore.

2.1.3 Cause and Effect Relationships

Comparison of the effluent and the nearfield water concentrations demonstrated that the mean concentrations in the St. Clair River reflect the effluent loads from the Cole drain and the Dow Chemical complex. The variability in the water concentrations near the outfalls was related to the variability in the effluent loads. The water data indicated that there were no major sources of the parameters of concern upstream from the Cole drain. The significant increase in the concentrations of the parameters of concern from the Cole drain to the Dow complex and the subsequent dilution of the contaminants downstream of the Dow complex indicated that these outfalls were the principle sources. Establishment of a cause and effect relationship is essential in the development of load allocation (effluent limit) procedures for specific outfalls.

2.2 Ambient Investigations

2.2.1 Water

Detectable levels of HCB, HCB_D, HCE, and mercury were observed in water samples from the Cole drain vicinity to as far as the mouth of the St. Clair River.

The measured concentrations of these substances, with the exception of mercury, adjacent to the outfalls were typically two to three orders of magnitude higher than "background levels" upstream from the Sarnia industrial complex. These measurements showed a high degree of variability, corresponding to the observed variability in effluent loads. Chemical concentrations in the river were observed to drop with increasing distance from the outfalls. For example, HCB ambient water concentrations at the Chenal Ecarte were approximately one order of magnitude lower than adjacent to the outfalls.

The conventional water-quality parameter chloride, is a readily measured compound indicative of inputs from the manufacture of industrial chemicals. This parameter may act as a useful indicator of the chemical dispersion of additional compounds with similar behaviour. Chloride concentrations on the U.S. side of the river, across from the Chenal Ecarte were approximately 1.5 times lower than those near the Chenal Ecarte, but slightly above the river background. This demonstrates that lateral mixing of the water and transboundary transport upstream of the River Delta are relatively minor.

This pattern appeared to be typical for a number of parameters and thus provides an indication of the "zone of impact". However, for mercury no significant differences were observed in ambient water concentrations between stations upstream and downstream from the selected outfalls.

Ambient water samples typically contained between 1.8 and 8.5 mg/L suspended solids, consisting of approximately 25% clay, 50% fine silt and 25% coarse silt. To distinguish between chemicals in aqueous solution and chemicals associated with particulate matter, ambient water samples from selected locations were centrifuged. This demonstrated that at the point of discharge, HCB, OCS and HCBd were almost entirely sorbed to suspended solids, whereas PERC was primarily in the dissolved form.

With increasing distance from the outfall, the fraction of chemical associated with suspended sediments was reduced substantially and the

fraction of dissolved chemical was increased. This indicates that in the receiving-waters, chemicals associated with suspended matter either tend to desorb and thus become available for uptake in aquatic organisms or that a dilution effect from clean suspended solids may occur. The centrifuging results indicate that by the time the discharge reaches the Suncor property, most of the contaminants are dissolved.

Water samples collected during May and October 1986 indicated a relatively uniform vertical distribution for most contaminants based on a comparison of surface and bottom water samples. Concentrations of the most hydrophobic substances HCB and OCS tended to be higher at the bottom (i.e. near the sediments) and lower near the surface. Concentrations of the less hydrophobic volatiles, e.g. CCL₄, tended to be higher near the surface and lower at the bottom. A possible explanation for this behaviour is that HCB and OCS were predominantly associated with particulate matter, which tend to settle to the bottom. The less hydrophobic volatiles such as CCL₄ were almost entirely in aqueous solution and thus followed the effluent plume. During most of the year the plume tended to rise towards the surface due to a higher effluent temperature than that of the ambient water.

As shown in Table 2, HCB concentrations in water samples exceeded PWQOs in up to 12% of the measurements. This occurred downstream from the Cole drain outfalls and at several stations downstream from the Dow 1st Street sewer outfalls. Water samples taken 1.1 km downstream from the Cole drain did not violate water quality objectives. PERC concentrations in ambient water samples exceeded the criteria established by the World Health Organization (10 µg/L) in up to 3.5% of the measurements, but did not exceed applicable guidelines for the protection of aquatic life. The MOE water quality advisory (a tentative and highly conservative value based on limited toxicological information) for OCS was exceeded in approximately 8% of the water samples. These samples were obtained adjacent to the Dow property. Water quality criteria for the other contaminants of concern were not exceeded. Due to the hydrophobic

TABLE 2: WATER QUALITY CRITERIA (WQC) AND FISH FLESH CRITERIA (FFC) AND MAXIMUM OBSERVED CRITERIA EXCEEDENCES (IN %) FOR PARAMETERS OF CONCERN IN WATER, FRESHWATER CLAMS AND JUVENILE FISH.

Superscripts refer to footnotes.

Parameters	WQC µg/L (ppb)	% Exceedence	FFC µg/kg (ppb)	% Exceedence			
		Water		Clams	Juv.	Carp	Catfish
HCB	0.0065 ¹	11.8%	330 ⁴	0%	0%	0%	0%
			6.4 ⁵	>0%	100%	100%	100%
			1.7		100	100	100
			0.36		100	100	100
			100 ⁶	0%	0%	0%	0%
HCE	1.3 ²	0%	14100 ⁴	0%			
CCL4	27 ²	0%					
PERC	260 ³	0%					
HCBd	0.1 ³	0.1%	1300 ⁴	0%	0%		
OCS	0.0001 ⁷	7.8%	20 ⁴	>0%	100%	100%	100%
2,4,5-TCT	0.134 ⁷	0%					

- (1) Ontario Ministry of the Environment, Provincial Water Quality Objective;
- (2) Guideline for the protection of aquatic life, Michigan Department of Natural Resources (MDNR);
- (3) Guideline for the protection of aquatic life, Canadian Council of Resource and Environment Ministers (CCREM);
- (4) Fish flesh criteria established by the New York State Dept. of Environmental Conservation (NYSDEC), for the protection of fish-eating wildlife;
- (5) U.S. EPA guideline for human consumption with an associated cancer risk of 10^{-6} (based on average consumption of 6.5 g fish/day). Additional values reflect consumption levels for average Ontario anglers (1.7 ppb) and high consumers (0.36 ppb);
- (6) Guideline by Health and Welfare Canada for the consumption of eggs with a 10^{-5} health risk.
- (7) Ontario Ministry of the Environment, Water Quality Advisory.

nature of OCS it is easily taken up by biological organisms and passed along the food chain. No definitive criteria were available from either MOE or other agencies for OCS. The water quality Advisory for OCS was developed by the Water Resources Branch of MOE using procedures outlined in "Ontario's Water Quality Objective Development Process" (MOE 1989). A final uncertainty factor of 6300, derived from an initial uncertainty factor of 10,000 which is assigned to extremely hydrophobic substances ($\log K_{ow} > 4$), was applied in developing an advisory of 0.1 ng/L for OCS. Chemicals which are less likely to concentrate in the biota (i.e. less hydrophobic with a $\log K_{ow} < 4$) are assigned an initial uncertainty factor of 1,000. The $\log K_{ow}$ is the log of the n-octanol/water partition coefficient. The solubility of a material in water decreases as the $\log K_{ow}$ increases. Additional toxicological information will enable the development of an Objective or Guideline with a lowered uncertainty factor and a higher degree of confidence. New information may result in a less stringent, more stringent or similar Objective/Guideline to the current advisory.

2.2.2 Sediments

(a) Contaminant Analysis of Sediments

Bed sediments were collected from the point at which the Cole drain discharges to the St. Clair River to downstream from the Lambton Generating Station. The composition of the bed sediments varied from gravel and sand to clay and silt and was heterogeneous in nature. Bed sediments were analyzed for physical characteristics, metals, chlorinated aromatics and volatiles.

Elevated levels of mercury were observed in nearshore sediments downstream from the Dow 1st Street and 2nd Street sewers, but dropped rapidly with increasing downstream and offshore distance. These measurements may reflect historical deposits from the early 70's when mercury was used in the manufacture of chlorine.

All organic contaminants analyzed in sediments obtained upstream from the Cole drain were generally below detection limits. Sediments in a region extending up to 1 km downstream from the Dow 1st Street Sewers were found to contain 1,3,5-tri-, 1,2,4-tri-, 1,2,3,4-tetra-, 1,2,4,5-tetra- and pentachlorobenzene (QCB), HCB, HCBd, OCS, HCE as well as PCBs. Further downstream, concentrations of these organic contaminants in sediments were again generally below or at the detection limit. The sediment data thus tend to confirm the major sources of contamination. The sediment samples exhibited elevated levels of total organic carbon (TOC), which exceeded the recommended MOE open-water disposal guideline of 10 mg/g.

(b) Sediment Transport

To obtain a better understanding of the contribution of various sources of contaminants to the bottom sediment contamination, an effort was made to quantify inputs from solids deposition. It was found that:

- (1) There is very little sediment accumulation in the entire river. Sediment cores collected in 1985 indicated that the top 3 cm of the sediment cores were less than 9 months old, the 3 to 8 and 8 to 13 cm intervals were 1 to 10 years old and the 13 to 18 and 18 to 24 cm intervals were 10 to 30 years old. This indicates that throughout most of the river, the sediments are dynamic and transitory with a river retention time of approximately 9 months to one year for the majority of bed material (Oliver 1988).
- (2) the quantity of bedload transport in the river is very small. In comparison, the transport of suspended sediment load is approximately 3 orders of magnitude greater than the bedload transport. It was estimated that the bedload transport accounts for less than 0.5% of the total contaminant load (Oliver 1988).

(c) Sediment Toxicity

Surficial sediment samples collected downstream from the Cole drain were acutely toxic to the bottom dwelling mayfly, Hexagenia limbata

(14% survival) and the fathead minnow, Pimephales promelas (67% survival). These results corresponded with field observations adjacent to Dow and Polysar which showed that benthic invertebrate populations were severely disrupted.

At Stag Island and further downstream, the survival of minnows was 100%; however, sediment samples collected between the Dow site and Sombra, Ontario exerted acute toxic effects on mayflies in the laboratory (up to 100% mortality). Survival of both minnows and mayflies was 100% at a station near the northern end of Walpole Island.

The compounds responsible for the low survival rate of the mayflies could not be positively determined; however, analytical results implicate visible oils and PAHs in the sediments as examples of possible causative agents.

The toxicity of the sediments to mayflies and minnows adjacent to the Dow property and mayflies in the interval from Dow to Sombra is in violation of Policy 5 of "Water Management: Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment" (MOE 1984), which states that no conditions within the mixing zone should be permitted which are rapidly lethal to important aquatic life.

Toxicity studies utilizing large volume effluent samples from Dow have indicated that undiluted effluent is not acutely toxic to Rainbow Trout.

2.2.3 Biota

Various aquatic biomonitors were utilized to (i) determine the body burdens and toxic response of absorbed contaminants for aquatic biota and (ii) to derive reliable values for the biomass of various organisms for modelling purposes. A compilation of the data for HCBD

is presented in Figure 3 as an example of body burden contaminant levels found in various biomonitors relative to levels in water and sediments from the same areas.

(a) Phytoplankton and Aquatic Plants

Elevated levels of most of the parameters of concern as well as PCBs were observed in phytoplankton samples collected in the vicinity of the Dow outfalls (Figure 1a). The phytoplankton biomass in the St. Clair River was estimated to be approximately 1.0 g/m^3 . The effects of contaminants on phytoplankton biomass were not investigated.

Measurable levels of OCS, HCB and HCBd were found in Cladophora as far downstream as Port Lambton.

Macrophytes collected along the upper St. Clair River, between Sarnia and Stag Island contained measurable levels of OCS, HCBd, QCB, HCB and the pesticide metabolites p'p'-DDE and heptachlorepoide. The total biomass of macrophytes in the St. Clair River was estimated to be 1663 tonnes when expressed on an ash free dry weight basis.

(b) Benthic Community and Contaminant Analysis

An investigation of the benthic invertebrate populations of the St. Clair River identified 7 major invertebrate assemblages or communities in the river. Upstream of Esso Chemical Canada Ltd., benthic invertebrate communities showed a large diversity of species characteristic of a healthy ecosystem. At the Polysar (Sarnia), Dow Chemical and Suncor sites, benthic communities were severely degraded. This was characterized by the dominance of pollution-tolerant species such as L. hoffmeisteri and Goniobasis (=Elimia), reduced species richness and low invertebrate density. This may be due to elevated concentrations of heavy metals in the sediments, oils and greases

and/or chlorinated hydrocarbons at these sites. From Suncor Inc. to Shell Canada Ltd. benthic communities were impaired but less degraded than at locations adjacent to the upstream industrial outfalls. Downstream from Shell Canada Ltd. to Polysar Ltd. (Corunna) benthic populations were degraded to severely degraded. Impaired benthic communities were found downstream from Polysar Ltd. (Corunna) as far as Allied Chemical Canada Ltd. Downstream of Allied Chemical, degradation of benthic communities was not observed. Based on this distribution, a zone of degraded environmental quality was identified along the Canadian shoreline from Esso Chemical to Allied Chemical. This impacted area is illustrated in Figure 2 and corresponds closely with the zone of elevated water and sediment concentrations for the 8 parameters of concern.

Measurements of the concentrations of HCB and OCS in the mayfly Hexagenia limbata and in the sediment at various locations along the river demonstrated that the body burden of the mayfly is correlated with the chemical concentrations in the sediments.

A comparison of the sediment and benthic study results suggests that there is a link between the presence of contaminants in the sediments, the uptake of these contaminants by benthic communities and adverse (toxic) effects to the benthos characterized by the absence of species. The benthic invertebrate fauna can thus be used as a measure of the effects of environmental stresses on aquatic systems.

The benthic community has improved substantially since the 1970's with a result that currently the impaired zone comprises 12 km of the river length along the the Ontario shoreline compared with the 21 km identified in 1977 (MOE 1979). The impaired zone corresponds closely to the contaminant plume predicted by the exposure models for 1984 to 1985 loading conditions. The model results indicate that with the 1986-1987 loads the impaired zone may be further reduced to approximately 6 km.

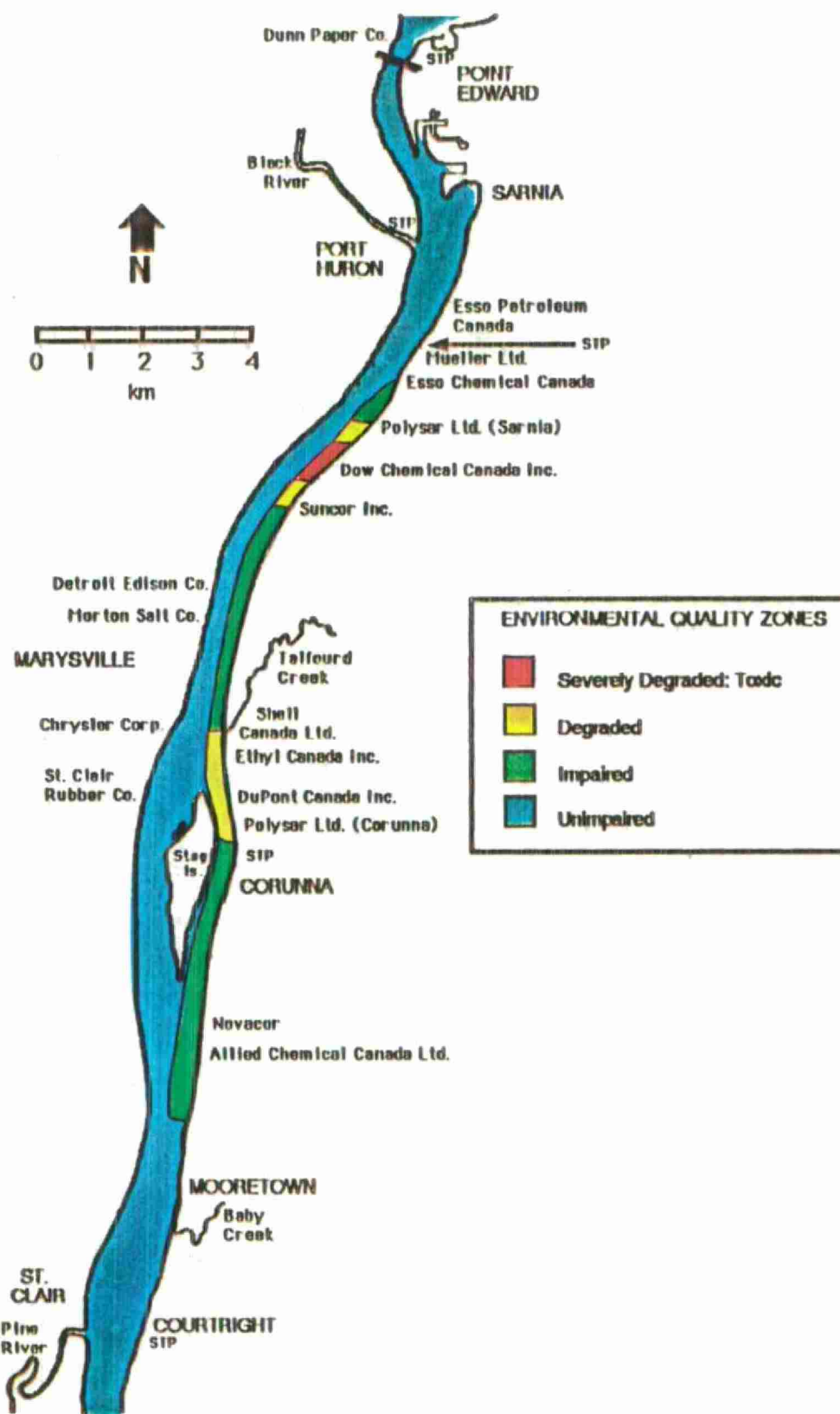
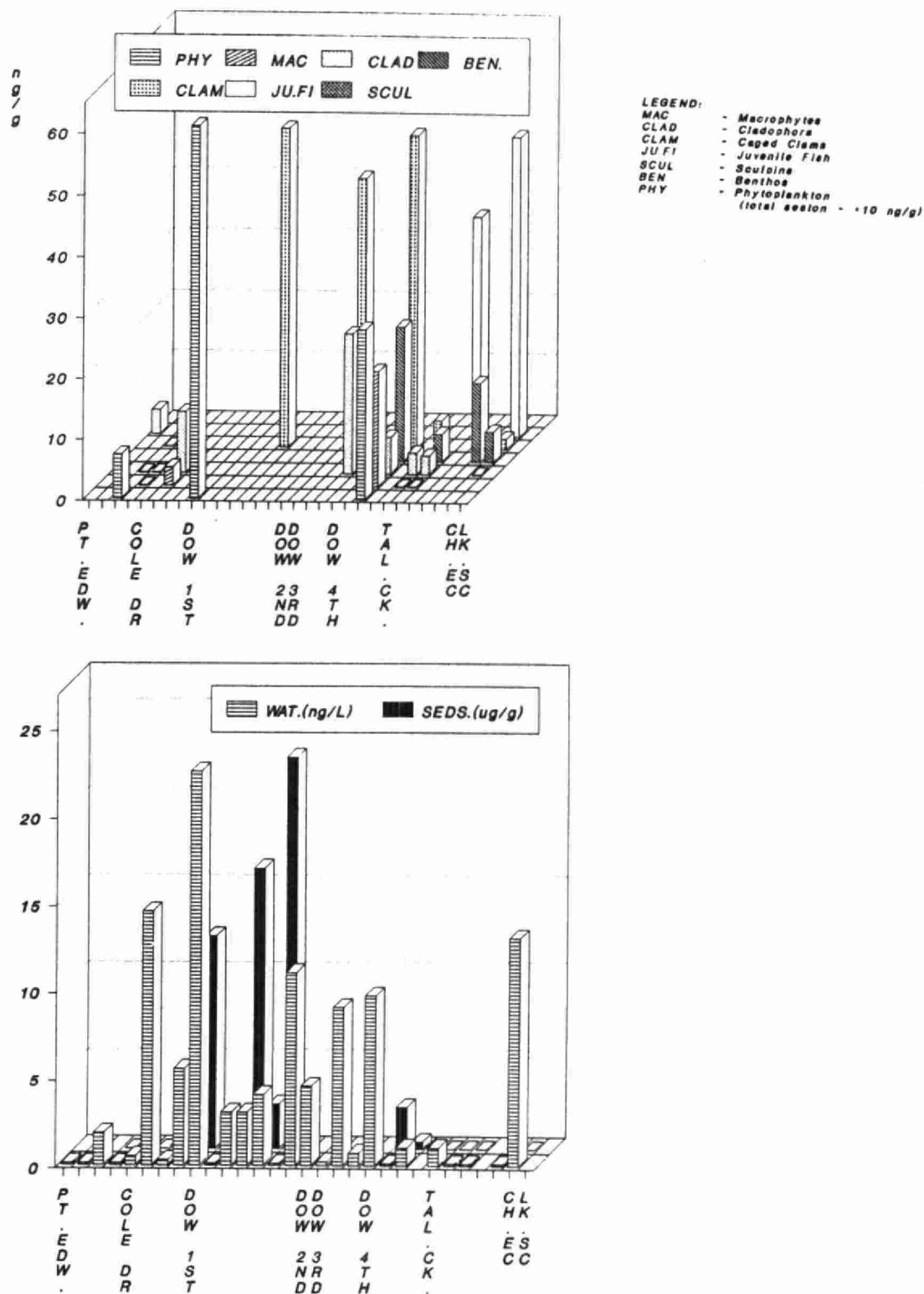


Figure 2: Environmental Quality Zones in the St. Clair River based on the distribution of Benthic Fauna.

Figure 3: Distribution of Hexachlorobutadiene in Water, Sediments, and Biomonitors along the Ontario Shoreline of the St. Clair River.



(Horizontal axis not to scale)

(c) Clams

A biomonitoring program using caged clams detected the highest levels of HCB, HCB, HCE and OCS in clam tissue in the river reach adjacent to Dow extending downstream from Suncor. Downstream from this point, the concentrations in caged clams dropped rapidly. Fish flesh criteria established by the New York State Department of Environmental Conservation for the protection of fish-eating wildlife were not exceeded, except for OCS. Several volatile organic compounds including benzene, chloroform, ethylbenzene and xylene were also observed in clam tissue.

At various stations, HCB concentrations in clams demonstrated the existence of a vertical gradient with higher tissue concentrations in clams exposed near the river bed and lower concentrations in clams exposed near the surface of the water. This may reflect the availability of HCB for uptake by the clam as a function of location in the water column. It demonstrates that the placement of the cages may have a considerable influence on the biomonitoring results; however, additional sampling will be required to confirm this.

(d) Young-of-the-Year Spottail Shiners

The results of a biomonitoring program with young-of-the-year spottail shiners and emerald shiners demonstrated that from 1985 to 1987, HCB concentrations in spottail shiners near the Lambton Generating Station have dropped by a factor of 3, indicating improved water quality conditions. During the same time period, no significant changes were observed for OCS. Throughout the course of the monitoring program, levels of OCS exceeded the 20 ng/g guideline (New York State guideline for the protection of fish-eating wildlife) for fish flesh in spottail shiners collected near Suncor Ltd., the Lambton Generating Station and in the South Channel.

(e) Sportfish

The sportfish monitoring program revealed no significant decline or increase in HCB and OCS body burdens for carp or channel catfish collected in Lake St. Clair. Channel catfish collected from this location were more contaminated than fish from the southern portion of Lake Huron; however, no consistent differences were noted for carp. The U.S. EPA guideline for human consumption with an associated cancer risk of 10^{-6} is 6.4 ppb for HCB. This guideline was exceeded in Lake St. Clair and St. Clair River carp and catfish. A less stringent guideline of 100 ppb for chicken eggs, set by Health and Welfare Canada to protect human consumers was not exceeded between 1985 and 1987. It should be noted that these guidelines are based on average U.S. or Canadian consumption levels. They do not apply to sensitive local groups (e.g. The Walpole Island First Nation Indians) or sport fishermen, who owing to their specific diet may be exposed to a larger quantity of potentially contaminated food items.

The average value of OCS in carp exceeded the New York State non-carcinogenic fish flesh guideline of 20 ppb for the protection of fish-eating wildlife in all years and at all locations in the St. Clair River and Lake St. Clair. Channel catfish exceeded the OCS guideline by a factor of 4 to 6 times in all years at the Lake St. Clair location.

2.3 Long-Term Effluent Monitoring

2.3.1 Loads and Long-Term Load Variability

The long-term (May 1986 - March 1987) contaminant loads were estimated based on randomly timed, twice-weekly samples. The average monthly loads were obtained as a product of (i) the mean of the twice-weekly concentrations obtained in any month and (ii) the mean monthly outfall discharge. These mean monthly loads were compiled for the period of May 1986 to March 1987. A high month to month variability was found in these data. For example, 5% of the time the mean monthly HCB loads exceeded 5 times the long-term mean load.

Table 3 shows the mean and the extreme loads for the parameters of concern. The extreme load is defined as the mean monthly load that is exceeded in 5% of the months. Table 4 indicates the presence of contaminants that occur in significant quantities at the investigated point sources.

2.3.2 Trends in Effluent Loads

Several trends are apparent in the data from the 11-month monitoring period ending in March 1987. There were reductions in the loads of OCS, HCB and HCBd from the Polysar 72-inch outfall. Mercury decreased at the Dow 54-inch sewer while HCB decreased at the Dow 3rd Street Sewer. HCE concentrations increased at the Dow 48-inch Sewer while CCL4 increased at the Dow 3rd Street Sewer. No significant trends in loadings of the other parameters of concern could be established during the May 1986 to March 1987 period. However, when these loads are compared with 1985 loads, there is a substantial decrease in many of the contaminants (DOE/MOE 1986; MOE 1987). Recent changes in effluent loadings have been affected by sewer diversions, the establishment of the Dow Block 90 pond during the latter half of the long-term monitoring study and on-going remedial improvements at Dow.

A comparison of the 1985 total loading of chlorinated aromatic compounds from the Dow complex of approximately 1 kg/d had decreased by approximately 75% by 1987. The total effluent loads from the Cole drain decreased during this period with the largest reduction occurring for 1,2,4-trichlorobenzene. Some contaminants, including HCB, increased at the Cole drain while decreasing at the Dow complex. OCS loadings increased at both the Cole drain and Dow outfalls. The total discharge of volatile compounds to the river decreased by approximately 90% between 1985 and 1987 at both the Cole drain and the Dow outfalls.

Dow self-monitoring data were consistent with Ministry data with respect to effluent variability and it is anticipated that on-going sampling as part of the MISA regulations will confirm effluent quality.

TABLE 3: OBSERVED MEAN MONTHLY LOADS 1986-1987

Mean Monthly Loads g/day								
SOURCE	OCS	HCB	2,4,5-TCT	HCBD	HCE	PERC	CCL4	Hg
COLE DRAIN								
MEAN	9.2	8.9	9.6	140	6.8	48	7.9	2.2
EXTREME	332	92	280	991	29	375	62	11.5
POLYSAR								
MEAN	3.1	0.1	.001	1	0.1	6.9	2.7	0.4
EXTREME	7.4	1	.004	7.1	0.4	54	21	20
DOW 1ST								
MEAN	3.5	7.5	50	31	80	2190	2972	4.4
EXTREME	8.3	31	165	130	3000	18000	22000	15
DOW 2ND								
MEAN	0.3	1.0	1.9	4	1.5	153	188	2.8
EXTREME	30	5.0	14.8	69	20	2500	622	62
DOW 3RD								
MEAN	0.1	0.1	0.2	1.9	0.4	25	254	2.7
EXTREME	16	0.5	3.7	125	1.0	370	1300	11.3
DOW 4TH								
MEAN	0.5	3.3	1.4	4.7	36	684	676	6.4
EXTREME	8.3	58	40	16	381	6600	2950	22

LEGEND:

OCS - Octachlorostyrene

HCB - Hexachlorobenzene

2,4,5-TCT - 2,4,5-Trichlorotoluene

HCBD- Hexachlorobutadiene

HCE - Hexachloroethane

PERC- Tetrachloroethylene

CCL4- Carbon tetrachloride

Hg - Mercury

Mean = Existing Mean Monthly load; Extreme = load exceeded in 5% of months.

Note: Polysar: Includes Biox and 72-inch outfalls.

Dow 1st: Includes 42-, 48- and 54-inch sewers

TABLE 4: PARAMETERS OF CONCERN THAT EXCEED 1% OF THE TOTAL LOAD
FROM POINT-SOURCES MONITORED DURING 1986-87

For Individual Contaminants

COLE DRAIN	OCS	HCB	2,4,5- TCT	HCBD	HCE	PERC	Hg	
POLYSAR 72-INCH & BIOX	OCS	Hg						
DOW 1ST STREET	OCS	HCB	2,4,5- TCT	HCBD	HCE	PERC	CCL4	Hg
DOW 2ND STREET	OCS	HCB	2,4,5- TCT	HCBD	PERC	CCL4	Hg	
DOW 3RD STREET	OCS	HCBD	CCL4	Hg				
DOW 4TH STREET	OCS	HCB	2,4,5- TCT	HCBD	HCE	PERC	CTC	Hg

Limited MOE data from Polysar (Sarnia) and Dow for 1988 do not indicate a significant change from the data collected in late 1986 and 1987 for the parameters of concern; however, continued improvements in waste treatment and cooling-water separation will likely result in gradually improved effluent quality.

3.0 LOAD ALLOCATION

3.1 Mixing Zone Definition

A mixing zone is defined in "Water Management: Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment" (the 'Blue Book' - MOE 1984) as "an area of water contiguous to a point source where the water quality does not comply with the Provincial Water Quality Objectives (PWQOs)". The 'Blue Book' indicates that this zone is to be "minimized to the greatest possible degree and may not be used as an alternative to adequate treatment". The purpose of a mixing zone is to protect aquatic life as well as other users. Policy 5 in the 'Blue Book' outlines the eleven conditions to be met within the boundary of a mixing zone. Limitations for mixing zones are to be established on a case-by-case basis with the size of a mixing zone limited by the nearest downstream user. Further, it is a requirement that the mixing zone should not be "a barrier to the migration of fish and aquatic life".

For the purpose of defining the mixing zone in this study for the Dow and Polysar outfalls and the Cole drain, it was recognized that fish will migrate near the bed in the nearshore regions of the river where the currents are reduced. Physical model studies, carried out at the University of Windsor (Abdel-Gawad 1985) on similar shore-based outfalls to those in this study, showed that the maximum plume impact on the bed occurred at between 4 and 10 times the river depth downstream of the outfall. This is based on the three dimensional nature of the slightly bouyant effluent plumes. Beyond this distance, the physical model showed that contaminants were mixed throughout the entire water column depth. For the purpose of this study, the length of the mixing zone was defined to be the shorter of 5 times the river depth or the distance to the next user (e.g. water

intake). Since the average depth outside of the St. Clair River shipping channel is about 6m, the established mixing zone length was 30m for shore-based outfalls. At its widest point, the expected mixing zone width would be 10m for shore-based outfalls and 20m for an offshore discharge (Abdel-Gawad and McCorquodale 1985).

The mixing zone is used in the allocation of loads for a particular outfall. The load is set so that the applicable guideline is satisfied at an acceptable compliance level at the edge of the mixing zone. Outside of this mixing zone there should be no long-term (chronic) effects on the aquatic life, in compliance with existing MOE policy. Within the mixing zone, the conditions should not be rapidly lethal to aquatic life.

3.2 Model Development

The allowable load is the load for which the defined objective will be satisfied for a specified fraction of the time at the edge of the mixing zone given the statistical variability of effluent quality. The more stringent the desired compliance target, the lower the allocated load. For the purposes of the load allocation computation, the selected fraction of the time that the objective is met is referred to as the compliance target. A monitoring plan must be designed and implemented in order to determine if the discharger is in compliance with the allocated load.

In this exercise, recommended allowable loads were based on a compliance target of 95%. In other words, effluent quality would only be allowed to be out of compliance 5% of the time. This is a practical level of compliance given current technology; however, one which may be subject to more restrictive levels in the future. A compliance target which is to be met 99% of the time would be at least one order of magnitude more restrictive than one to be met only 50% of the time. A compliance target of 100% would be essentially zero discharge.

Load allocations are very sensitive to variability in effluent quality. Intermittent peaks may account for a large proportion of annual contaminant loadings, while occurring only briefly. Load allocations are established considering these peaks and their statistically predicted frequency of

occurrence. If point-source control of these peak discharges could be achieved, current median loadings for many contaminants would be at or near modified recommended compliance levels.

The following models were developed to assist in relating contaminant loads to the concentrations of the contaminant in various parts of the ecosystem:

(1) Dynamic Exposure Model

The WASTOX exposure model considers the river and/or lake system in terms of a number of 3-dimensional cells which represent the upper water, lower water, active bed, and deep bed components of the system. A mass balance is applied to each cell and to the system as a whole. The factors considered in the mass balance include: point-source loads, river currents, non point-source loads, advective transport, dispersion, diffusion, volatilization, biodegradation, photolysis, hydrolysis, oxidation, partitioning, and sediment transport.

(2) Dynamic Food Chain Model

The food chain submodel of WASTOX is an unsteady state multitrophic level model which considers resident and migratory species. The model used in this study was developed based on input at the 1987 MOE Aquatic Food Chain Workshop (MOE 1988). The model included benthic invertebrates, benthic fish, phytoplankton, two age classes of zooplankton, small fish and adult fish of up to 7 age classes. This model was calibrated based on MOE fish data for Lake St. Clair using loadings of HCB and OCS based on data collected prior to the MISA investigation.

(3) Steady state Exposure Model

The KETOX model is a steady state model which was developed to provide high resolution predictions of contaminant levels in the vicinity of specific outfalls. Volatilization was found to be the main loss mechanism for contaminants in the river.

(4) Generic Food Chain Model

The Thomann Generic Food Chain model is a four trophic level steady state model based on biota size; the selected levels are representative of phytoplankton, zooplankton, small fish and large fish.

3.2.1 Model Evaluation

Table 5 provides a critical review of the models that were used in this study. In spite of the limitations that have been outlined for the exposure models, the calibration errors are relatively low in comparison with uncertainties associated with load variation. The aspects of these models most in need of improvement are:

- (1) near-field processes including buoyancy effects;
- (2) the sorption/desorption simulation;
- (3) the water column bed sediment exchange process;
- (4) rate constants and partitioning coefficients for various bed sediments;
- (5) inclusion of a stochastic component in the model to describe concentration fluctuations as well as spatial variations due to the heterogeneous nature of the bed.

It is important to note that modelling is the only way in which hypothetical load-ambient concentration relations can be developed for specific contaminants; these relationships are essential for the allocation of loads. Modelling is, therefore, an indispensable tool in the derivation of receiving-water-Based effluent limits. The weaknesses alluded to in the biota and sediment components of the models are related to the complexity of these systems as well as the extensive data requirements for proper calibration and verification

Current MOE initiatives for future enhancements of the food chain models will involve the use of microcosm studies. These studies will establish site and species specific rate constants that will improve

TABLE 5: EVALUATION OF MODELS USED IN DETERMINING WASTE LOAD ALLOCATIONS

MODEL	ADVANTAGE	DISADVANTAGE
WASTOX Exposure	Dynamic (unsteady). Multilayered. Portable to other rivers and lakes. Flexible framework. Bed load included. System response tool.	Poor spatial resolution. Instantaneous phase partitioning. Site calibration essential. Long computation.
WASTOX Food chain	Dynamic. Flexible. Portable. System response tool.	Time response needs work. High data requirements. Needs site calibration.
KETOX Exposure	High spatial resolution. Complete hydrodynamics. Fast computation time. Treats complex river systems. Portable to other rivers. Load allocation tool.	Steady state. Instantaneous phase partitioning. Depth averaged concentrations. Site calibration advised.
THOMANN Food chain	Simple. Fast computation time. Easy calibration. Screening tool.	Steady state. Site calibration advised.

the reliability of the models in predicting body burdens. The microcosm studies would also provide information on seasonal effects such as water temperature and biomass fluctuations. Future models should account for the short-term and long-term concentration fluctuations in the water column.

3.3 Load Allocation Procedures

The predictive accuracy of the exposure models depends mainly on three factors: (i) the calibration error of the model, (ii) the river flow and (iii) the contaminant mass loadings from the outfalls. All of these factors are of a stochastic nature; that is, governed by the laws of probability. Most of the difference between the actual concentration and the predicted concentration can be accounted for by a combination of the variances in these factors. In order to assure a certain level of compliance to meet environmental criteria, a statistical procedure was developed to treat the load responses of the water, sediment and biota. In order of importance, in setting loads based on water-quality and biota criteria, the load variation was the highest and the flow variation was the lowest. In the case of the bed sediments the model calibration error was large and of similar importance to the load variation.

The sequential and long-term effluent monitoring field studies revealed that loads have both hourly and monthly variations. The hourly variation (less than 1/2 hour) is far more severe than the monthly fluctuations. For the purposes of the load allocation in this study, the load variance was based on the monthly fluctuations since the bed sediments and the higher trophic levels of the food chain have response times in excess of 1 month (Gobas and McCorquodale 1989). The monthly variance is appropriate when the concern is chronic effects. It should be noted that other users may require consideration of the hourly variance in loads (e.g. for drinking water intakes, the hourly variance would be appropriate). In addition, the effluent at no time should be acutely toxic (i.e. exceed the 96-hour LC_{50}) to biota.

Load allocation procedures were developed for environmental criteria established for acceptable water concentrations, sediment concentrations and body burden in the biota. In the determination of the allowable loads it was assumed that a compliance level of 95% should be achieved based on the mean monthly loads. The 95% compliance level and the monitoring to assess compliance was suggested by Sharma et al. (1989). Considering variances associated with loads, river flows and model calibration, the appropriate model was used to estimate the allowable load to meet the criteria at the edge of the mixing zone for the specified compliance level. The allocation is repeated for each outfall and for each parameter of concern.

Table 1 shows the derived load limits at a 95% compliance level for the Cole drain, Polysar, and Dow Outfalls for the parameters of concern. Detailed load allocation results for both 50 and 95% compliance levels as well as preliminary biota and sediment based load allocations results were also calculated; however, only the 95% compliance loads are presented. The 95% compliance load was much lower than the 50% compliance load, due mainly to the high variability in the mean monthly loads.

Recommended allowable loads reflect the lesser of existing loads or the predicted load based on modelling results. Recommended reductions vary from 0% for a number of compounds including HCE, CCL4 and mercury, to greater than 99% reductions for OCS at all outfalls. Recommended reductions for other parameters of concern evaluated include 0-88% (HCB); 0-32% (2,4,5-TCT); 0-38% (HCBd) and 0-54% for tetrachloroethylene (PERC).

3.4 Management Implications of Load Allocation Procedure

An increase in the size of the defined mixing zone will result in an increase in the load allocated to an outfall. Conversely, if the mixing zone is reduced, the allocated loads to meet criteria will have to be decreased. Predictive modelling indicates that a 100 per cent increase in the mixing zone length will permit a 25 per cent increase in the allowable load; a 50 per cent decrease in the length of the mixing zone will yield a 50 per cent reduction in the allocated loads if the PWQO is the limiting

criterion. However, it must be remembered that an increase in the mixing zone and the associated increase in the allocated load will result in an increased risk of damage to the ecosystem.

The magnitude of the effect of the compliance target on the load allocation depends on the specific outfall as well as the parameter of concern. For example, for HCB at the Dow 1st Street Sewer complex, the load for 95 per cent compliance (i.e. out of compliance 5 per cent of the time) on a monthly basis is 1/5 of the load for 50 per cent compliance. The 99 per cent compliance load would be 1/10 of the 50 per cent compliance load. Thus, an increase in the compliance target results in a decrease in the allowable load.

The allocated loads can be based on individual samples or an average of several samples. The mean monthly data used in this study represent an average of 8 or 9 samples. Since there was a greater variability amongst the individual samples than the monthly averages, a compliance criterion based on individual samples would give lower allocated loads. At 95 per cent compliance at the Dow 1st Street Sewer complex for HCB, the allocated load is 7 per cent of the average load if individual samples are used and 16 per cent of the average load if monthly averaged data are used. It is important to consider the response of the ecosystem compartment when determining the appropriate averaging period. The period of one month was used because this is consistent with the accumulation response times for biota and bed sediments. If the concern is acute toxicity or the protection of drinking water supplies, then the individual sample (instantaneous data) should be used in allocating loads.

4.0 CRITIQUE OF ASSESSMENT TECHNIQUES

4.1 Component Utility in Setting Effluent Limits

Models were used to estimate loads that will ensure an agreed upon compliance based on acceptable receiving-water quality. Table 6 provides details of the utility of various sampling components in setting effluent

TABLE 6: UTILITY OF VARIOUS TECHNIQUES FOR ESTABLISHING EFFLUENT LIMITS

Technique	Water-Based Load Limits	Sediment-Based Load Limits	Biota-Based Load Limits
EFFLUENT CHEMISTRY:			
Sequential sampling	Essential A	Essential A	Essential A
Effluent chemistry: Long-term monitoring	Essential B	Essential B	Essential B
Effluent toxicity	- A	- A	- A
AMBIENT WATER CHEMISTRY:			
Sequential sampling	Essential A	-	-
Investigative sampling	Essential A	Essential A	Essential A
Centrifuging	Supportive A	Supportive A	Supportive A
BIOLOGICAL MONITORING:			
Bacteria	- -	- -	- Non-essential
Benthic enumeration	-	-	Non-essential A
Contaminant residues in phytoplankton	-	Supportive B	Supportive B
Macrophytes	-	-	Non-essential A
<u>Cladophora</u>	-	-	Supportive A
Benthos	-	Supportive B	Supportive B

TABLE 6 (cont'd):

Technique	Water-Based Load Limits	Sediment-Based Load Limits	Biota-Based Load Limits
BIOLOGICAL MONITORING:			
Sculpins	-	-	Supportive C
Juvenile fish	Supportive C	- -	Supportive C
Sport fish	-	-	Essential C
Caged Clams	-	Essential C	Supportive B
SEDIMENT SAMPLING:			
Sediment chemistry	-	Essential C	Essential C
Sediment toxicity	-	-	-

Level of effort expended in study:

A = more than adequate

B = adequate

C = inadequate. More information needed.

- = not used

limits. The following components of the study were used for calibration, verification and/or validation of the various models used in the load allocation procedure:

- (1) Data from the sequential effluent and ambient sampling;
- (2) Long-term effluent monitoring data which established the monthly loads and variability;
- (3) Ambient investigative data including:
 - a) Water sampling,
 - b) Bed sediment data,
 - c) Suspended material data (filtered seston as well as centrifuging data),
 - d) Clam data,
 - e) Young-of-the-year fish data,
 - f) Sportfish data,
 - g) Benthic invertebrates,
 - h) Plankton data.

The effluent toxicity studies were not used directly in the model development; however, the environmental criteria which ultimately determine the allowable loads are related in some cases to the toxicity levels. Further, toxicity evaluations enable the determination of "never to exceed" contaminant levels.

4.2 Component Utility in Defining Environmental Impact

The benthic enumeration component indicated that a zone of the St. Clair River along the Canadian shore from Esso Chemical Canada Ltd. to the village of Mooretown is biologically impaired; this zone corresponds closely to the plume of contaminants predicted by the WASTOX and KETOX models. In addition to demonstrating the existence and extent of the contaminant impact, the benthic studies are useful in setting a baseline against which future remedial actions can be evaluated.

Studies such as the bacterial slimes, Cladophora and macrophytes were not essential to setting effluent limits nor to defining the problem; however, these studies did provide data on the ecosystem which will doubtless be used to improve ecologically based models in the future. These studies may help to answer questions relating to the role of bacteria in the biodegradation of in-place pollutants and the role of macrophytes in the temporary storage and release of contaminants.

4.3 Component Utility in Monitoring for Compliance

The statistical characteristics of the effluent loads as established by the sequential and long-term effluent monitoring program of this study provide the basis for designing a compliance monitoring protocol. In addition, the data obtained will enable environmental managers to set priorities for remedial action.

4.4 Cost Effectiveness of Components

Effluent monitoring, both short- and long-term, is essential to reliable load allocation. River water sampling both upstream and downstream of the potential sources is also an essential component of a load allocation procedure. It is important that the water sampling be coordinated with the effluent sampling. Other studies should include a systematic survey of the bed sediments, upstream and downstream of possible sources. The use of caged clams and young-of-the-year fish is an effective means of evaluating the spatial and temporal trends in the river. Finally, mathematical modelling is the most cost-effective method of utilizing the field data to infer system behaviour and to set loads based on environmental criteria and compliance protocols.

4.5 Transferability of Methodology or Study Component

This study was designed to make methodologies readily transferable to other sites. The study components listed in Section 4.1 are all transferable to other sites with a similar industrial base including petrochemical industries which discharge to a connecting channel environment.

The models and the load allocation procedures developed in this study can be applied to any other connecting channel in the Great Lakes system; however, site specific calibration will be required. The KETOX model is specifically for rivers in which lateral mixing is an important factor. The WASTOX models can be used in both river and lake environments. The KETOX and Thomann models proved to be more useful than the WASTOX models in load allocation because of their better spatial resolution. The WASTOX type of model is required for dynamic conditions, for example those that involve in-place pollutants. The WASTOX model used in conjunction with other models would be best suited for a lake or other receiving environment.

While some of these models may be appropriate for lake environments on their own, this unique combination of models selected for the St. Clair River was determined to be best suited for an environment such as a Great Lakes connecting channel.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Waste Load Allocation

- Mixing zones for the Cole drain, Polysar (Sarnia) outfalls and the Dow Chemical sewers have been delineated in accordance with Policy 5 of the MOE 'Blue Book'. Water-, sediment-, and contaminant residue in biota criteria were used to estimate allowable receiving-water-based effluent loads for all of the point sources in this study. The water-quality-based load allocations were more reliable than the sediment- and biota-based allocations due to a lower calibration error and more complete data than for both the sediment and food chain components of the model.
- As such, recommended maximum permitted loads (Table 1) were derived from the MOE Provincial Water Quality Objectives for mercury and hexachlorobenzene; water quality Advisories for OCS and 2,4,5- TCT; and criteria endorsed by outside agencies for other parameters of concern.

- The results of this study indicate that reductions in load variability would be an effective means of achieving a desired level of compliance with criteria.

The water-quality-based permitted loads may be less restrictive than biota- and sediment-based loads (e.g. Biota - HCB and OCS; sediments - Hg); however, until food-chain and sediment-based models undergo refinements, and adequate site-specific databases are developed.

It is recommended that:

- (1) The maximum allowable water-quality-based loads for specific sewers at Dow and Polysar, as well as the Cole drain (Table 1) be considered to maintain acceptable environmental conditions at the mixing zone perimeter.
- (2) Continued efforts must be expended to develop PWQOs for those parameters of concern for which there are currently no MOE endorsed Objectives. The availability of toxicity data through ongoing and proposed government and industry initiatives will enable the development of PWQO's and PWQG's with a higher degree of confidence and more appropriate safety factors.
- (3) Additional data and model refinements be incorporated into existing food-chain and sediment-based models to:
 - i) further refine the model and
 - ii) develop biological- and sediment-based effluent limits to ensure adequate protection of the environment.
- (4) Provincial sediment quality guidelines and contaminant residue in biota guidelines require timely development to allow maximum use of sediment and biota data in fate and transport models and in determining effluent limits.
- (5) Priority consideration must be given to the development of biota-based load allocations to protect the general population, with special

consideration to local communities, such as the Walpole Island First Nation Indian Community, consuming large quantities of locally caught fish.

5.2 Utility of Assessment Techniques for Establishing Effluent Limits

- The following assessment techniques were essential for setting water-quality-based effluent limits.
 - Ambient water sampling; Sequential sampling; Long-term effluent monitoring;
 - Juvenile fish and centrifuging data provided necessary data in support of the model calibration.
- Although the water-quality-based model is currently more reliable for setting load allocations than sediment- and biota-based models, these latter assessment techniques are necessary to determine the effectiveness of remedial measures and will ultimately be applied with similar confidence to the present-day water-quality-based models.

5.3 Long-Term Effluent Monitoring

- Contaminant loadings from Dow Chemical to the St. Clair River have been substantially reduced since November 1985. Reductions between November 1985 and the 1986-87 study period were on the order of 76% for chlorinated aromatic compounds and 90% for volatile organic compounds. Before additive facility loadings can be adequately documented for the Dow complex, the effect of the re-direction of effluent streams into the Block 90 pond requires further investigation. It is recommended that:
Additional effluent monitoring data arising from the MISA Effluent Monitoring Regulation should be evaluated to:
 - (i) verify sewer and facility load reductions to the St. Clair River;

- (ii) evaluate the effectiveness of specific in-plant remedial measures;
- (iii) assess the environmental impact of chemical discharges to the Block 90 Pond.

- Long-term effluent monitoring indicated that both the Cole drain and the Dow 42-inch sewer are significant sources of the parameters of concern, including HCB, HCBd, HCE and OCS. It is recommended that: **Specific remedial measures for reducing loadings of these contaminants to the St. Clair River must be undertaken in the Cole drain catchment basin and in the waste streams entering the 42-inch sewer in order to achieve the recommended water-quality-based load allocations.**

5.4 Sequential Sampling

- Sequential sampling demonstrated large and frequent fluctuations of chemical concentrations in all sampled sewers at Dow, Polysar (Sarnia) and the Cole drain. This may have considerable implications for the establishment of relationships between the discharged load and the resulting body burdens in biota, toxicity and criteria violations at the edge of the mixing zone. It is recommended that: **The role of load variations on chemical bioaccumulation be investigated with consideration given to the effects of pulse toxicity and/or the instantaneous uptake of contaminants by biological organisms.**
- The WASTOX model was capable of reproducing the relationship between ambient concentrations and loads. Temperature differences between the river and the effluent resulted in buoyant plume effects. It is recommended that: **Buoyancy and settling effects should be incorporated in future applications using the WASTOX model.**

5.5 Centrifugation

- Centrifugation studies showed that HCB, HCBd and OCS were primarily sorbed to suspended solids at the point of discharge, while further

downstream a larger fraction of the contaminant was in aqueous solution and therefore biologically available. At the outfall and further downstream, PERC was primarily in solution. It is recommended that: **Since centrifugation is time consuming and costly, alternative methods for determining the partitioning of sorbed versus dissolved chemical should be investigated.**

5.6 Investigative Water Sampling

- Elevated contaminant levels in the whole water were mainly confined to a relatively narrow zone adjacent to Dow and Polysar (Sarnia); however, exceedences of the PWQO for HCB (i.e. 6.5 ng/L) occurred as far as 1200m downstream of the Dow 1st Street sewers and in 12% of all water samples. Other parameters of concern including HCBd, OCS and PERC violated water quality objectives in 0.1 to 7.8 % of samples obtained (Table 2). These exceedences occurred primarily from the Polysar (Sarnia) and Dow vicinity to Suncor.
- Model calibration and verification was difficult for some compounds, in particular volatiles, since the measured ambient water concentrations were near the method detection limit of approximately 1 µg/L (1 ppb). It is recommended that:
Research for the continued development of practical methods for low-level detection of contaminants, especially volatiles, should be encouraged.

5.7. Sediment Contaminant Distribution

- Levels of various metals and organics were elevated in the vicinity of the Dow 1st Street outfalls. While sediment samples indicated a very heterogeneous matrix, levels of HCB in 1986 may be somewhat reduced over levels in 1985. It is recommended that:
Due to the heterogeneous nature of sediments in the St. Clair River, it is recommended that a more intensive sampling effort should be undertaken. This will better document the spatial and temporal

distribution of contaminants thereby improving confidence in sediment-based waste load allocation procedures and results.

5.8. Sediment Toxicity

- HCB and OCS concentrations in benthic invertebrates and sediments tend to correlate. Sediments collected in the vicinity of the Dow 1st Street sewers were acutely toxic to fathead minnows and mayflies. It is recommended that:

These parameters be given priority consideration in the development of sediment- and biologically-based guidelines. Benthic community organisms should be evaluated for use as indicators for compliance in meeting mixing zone requirements.

5.9. Biological Monitoring

- At the St. Clair River Pilot Site, young-of-the-year fish were useful in the development of water-quality-based load allocations as they reflected the observed loading trends for HCB and OCS.
- Biomonitoring data indicate that the benthic community has improved substantially since the late 1970's resulting in a reduction of the "impaired" zone from 21 to 12 km downstream from the Polysar/Dow site. Based on 1986-87 effluent loads, modelling results indicate that the impaired zone may be further reduced to approximately 6 km.
- Caged clams serve as useful biomonitors in specific areas. However, the St. Clair river has proven to be less than optimal for the recovery of introduced clams due to the river's strong currents and interference from users of the river.
- Average levels of HCB in sportfish samples collected in 1985-1987 did not exceed a human health guideline established by Health and Welfare Canada for the consumption of whole chicken eggs; however, carp and channel catfish collected from Lake St. Clair exceeded existing U.S. EPA consumption guidelines for the protection of human health.

It is recommended that:

- (1) In addition to the on-going sportfish contaminant testing program, regular biomonitoring of the benthic community and young-of-the-year fish are to be continued to document the effectiveness of further remedial measures.
- (2) The use and significance of several biomonitoring methods, which included heterotrophic bacteria, bacterial slimes, phytoplankton and macrophytes, need to be evaluated and improved by:
 - (i) Developing consistent protocols for deployment conditions, deployment times, chemical analysis considering total and bioavailable contaminant concentrations, quality assurance and monitoring of environmental variables (e.g. temperature, oxygen content).
 - (ii) Developing methods which allow a quantitative interpretation of biomonitoring results. These methods should enable body burdens in biomonitors to be translated to bioavailable chemical concentrations in the water and/or sediments, which can then be interpreted in terms of loads.

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